

## **PROGRESS OF BLM-FUNDED ACID MINE DRAINAGE RESEARCH**

**W. W. White III**, Physical Scientist, U.S. Bureau of Land Management, Salt Lake Field Office

**Kim A. Lapakko**, Principal Engineer, Minnesota Dept. of Natural Resources, Lands and Minerals Division

**Edward M. Trujillo**, Associate Professor, University of Utah, Chemical and Fuels Engineering Department

### **ABSTRACT**

The environmentally sound management of abandoned, existing, and future metal mine wastes on public lands has been identified as the most difficult and costly reclamation problem facing federal and state land-managing agencies. Drainage-quality prediction is essential to environmentally sound mine-waste management. The U.S. Bureau of Land Management (BLM), in association with the Minnesota Department of Natural Resources Division of Lands and Minerals (MN DNR) and University of Utah Chemical and Fuels Engineering Department (University), continued sponsorship of research on predictive modeling of contaminated drainage from metal-mine waste after the U.S. Bureau of Mines closed.

A well-defined kinetic test protocol was developed and approved as an ASTM method with funding from the USBM and the BLM. BLM-sponsored research showed that the ASTM humidity-cell protocol produced highly reproducible drainage quality, within and among laboratories, on four waste-rock lithologies (MN DNR). A simplified humidity-cell method produced results similar to those from the ASTM protocol with comparable intralaboratory replication. Mine-waste characterization and accelerated-weathering (humidity cell tests ranging from 20 to 278 weeks) were conducted on 63 samples from eight different mine-waste lithologies (MN DNR). For three lithologies with at least moderate amounts of calcium and magnesium carbonates, 24 to 60 percent of the neutralizing carbonates were available in samples with neutralization potentials of 21 to 42 g  $\text{CaCO}_3$  (kg rock)<sup>-1</sup>. Acid production thresholds were identified based on the sulfur content of two mine-waste lithologies with very low calcium and magnesium carbonate contents. Drainage pH values less than 4.5 were produced by Duluth Complex samples with  $\text{S} \geq 0.41\%$  and field test piles yielded drainage pH values similar to laboratory values for samples of similar sulfur content. Drainage pH values less than 4.5 were also produced by Archean greenstone samples with  $\text{S} \geq 0.2\%$ . Field rates of chemical release from Duluth Complex and Archean greenstone rocks typically ranged from 10 to 45 percent of those for laboratory samples of similar sulfur content.

The University's laboratory model demonstrated reasonable agreement between modeled output and actual pH, sulfate, and calcium concentrations from weekly humidity-cell drainage produced from accelerated weathering of five different waste-rock lithologies. The field model linked governing geochemical reactions to transport phenomena in porous media and produced concentration profiles for multiple species in a simulated symmetrical test pile.

Results from the BLM-sponsored research are published in 5 peer-reviewed journal papers, 2 M.S. theses, and 19 contract reports.

## **INTRODUCTION**

### **Significance and Need for Continued Research**

Generation of contaminated drainage from abandoned, existing, and future mine sites has been identified by the US Forest Service (USFS) “as the most difficult and costly reclamation problem it faces with western metalliferous mining operations” (USFS 1993). According to the Abandoned Mine Land Task Force (1996), more than 100,000 abandoned mines in the western U.S. are located on BLM and USFS lands; additionally, several thousand are reported on National Park Service (NPS) lands. Based on state 303(d) listings of affected streams, as many as 15,910 miles of stream length have been affected by contaminated drainage from metal-mining activities. USFS (1993) also identified more than 1500 mining sites on National Forest Lands that have been affected by contaminated drainage. Contaminated drainage adversely affects water quality, damages aquatic and riparian habitats, and consequently has the potential to impact wildlife and human health, and limit use and enjoyment of some of the more scenic portions of the Public Lands.

Federal and state land-managing agencies are (and will continue to be) challenged with making environmentally-sound decisions on how to best manage millions of tons of mine waste from abandoned, existing, and future metal-mining activities without adversely impacting existing surface and groundwater quality. Abandoned-mine wastes can produce drainage that is neutral for years and then acidifies. Based on neutral drainage observed in the field, remediation of such wastes may be ignored. However, subsequent generation of acidic drainage could result in severe impacts to water quality. Thus, without knowledge of future drainage quality, a mine waste with potential to adversely impact drainage quality for decades might be left unremediated, while financial resources were expended toward reclaiming less reactive wastes.

Mine-waste management decisions for developing mines are largely based on the predicted quality of drainage from the mine waste. While suites of laboratory-predictive tests and their results are commonly used by industry and reviewed by land-managing agencies to help forecast mine-waste drainage quality, no consensus exists regarding how well these tests predict future drainage quality in the field. Because of the complexity of the problem and the uncertainty of predictive-test accuracy, land-managing agencies are most concerned that decisions made in good faith today will return to haunt them in future. USFS (1993) acknowledged that “technical uncertainties are associated with the prediction of acid drainage potential at the time of mine plan approval.” The agencies want to solve the contaminated-drainage problem, not add to it by making improper decisions on mine-waste management due to errors in drainage quality prediction. Their major concern is the prospect of having contaminated drainage develop 25 to 50 years in the future from mine-waste tonnages that they allowed to be placed on public lands based on their current level of knowledge.

To avoid such a scenario, BLM, USFS, and NPS need reliable laboratory predictive tests, a systematic compilation of predictive test data, and predictive mathematical models that reliably forecast mine waste drainage quality. These components are essential for making scientifically based decisions on the environmentally-sound management of mine wastes from abandoned, existing, and future mines. They are also the focus of the current BLM-sponsored research.

## **Research Chronology**

Federally-sponsored research to predict drainage quality from waste rock associated with U.S. metal mining has been conducted since October 1990 (beginning of Fiscal Year 1991), and continues today. U.S. Bureau of Mines sponsored the research for 5 years, and U.S. Bureau of Land management continued sponsorship of the research after closure of the Bureau of Mines in 1996.

### ***Bureau of Mines Sponsored Research (1991-1996)***

Acid-Rock Drainage (ARD) prediction research was initiated by the U.S. Bureau of Mines Salt Lake Research Center (USBM), and was conducted jointly with University of Utah Chemical and Fuels Engineering Dept. (University), and Minnesota Dept. of Natural Resources (MN DNR) from October 1990 to the end of January 1996 when the USBM was abolished by Congress.

Two components comprised the research, kinetic testing and mathematical modeling. Kinetic testing provided empirical data on the variation of drainage quality as a function of compositional variations within individual mine-waste lithologies. This information also provided the empirical database required for the calibration of the developing mathematical predictive models. The kinetic or laboratory accelerated-weathering and field test-pile testing were conducted by MN DNR and USBM, and the mathematical predictive modeling was performed by the University. The broad objectives of the research were to 1) identify and describe the chemical reactions that govern the formation of ARD from samples of metal-mine waste rock subjected to accelerated weathering in laboratory humidity-cell experiments, 2) develop geochemical-kinetic models that would predict the rate of acid generation and trace-metals release in drainage from metal-mine waste rock, and 3) calibrate the developing models by matching modeled output with experimental data from humidity-cell tests and drainage from waste-rock test piles.

By early 1996, USBM had invested nearly \$1.5 million in this research (USBM 1995, p. 138).

Research products included: 1) up to 4 years of empirical data from laboratory accelerated-weathering tests of ten samples from two different rock types, 2) an American Society for Testing and Materials (ASTM) standard method (D-5744-96) for accelerated weathering of mine-waste samples in a modified humidity cell, and 3) two preliminary geochemical-predictive models. The models included a laboratory humidity-cell model and a field test-pile model (Lin 1996; Lin and others 1997; White and Jeffers 1994; White and others 1994). At this point, the laboratory humidity-cell model had been calibrated with experimental data from two different waste-rock lithologies, and the field test-pile model had been mathematically tested but not calibrated.

### ***Bureau of Land Management Sponsored Research (1997-present)***

When Congress abolished the USBM in early 1996, the ARD-prediction research was transferred to the Bureau of Land Management (BLM) Utah State Office (USO) with limited funding of \$125,000. USBM's objective was to enable limited research to continue until September 30, 1996 so that the project database could be preserved and some conclusions published. Because BLM considered ARD to be one of its land-management priorities, USO decided to continue the research and provided a total of \$308,000 to the project from October 1, 1996 through September 30, 2001

(Fiscal Years 1997-2001). MN DNR also contributed \$338,000 during 1998-2001 to support humidity-cell experiments and the construction and sampling of four waste-rock test piles.

In addition to BLM and MN DNR funding, American Assay Laboratories (AAL) and a private mining company have provided nearly 5 years of humidity-cell testing and samples of metal-mine waste rock. AAL's cost to test five samples for 5 years was \$90,000 to \$100,000. The private mining company's contribution was approximately \$15,000. This combination of BLM and MN DNR funding and private-industry "in-kind" support has totaled about \$746,000 since October 1, 1996, and has enabled University and MN DNR to continue the joint research that was originally started with USBM to benefit the land managing agencies.

Currently, 63 samples from 8 different waste-rock lithologies have been subjected to accelerated-weathering tests in modified humidity cells. Periods of record for these laboratory tests ranged from 20 to 278 weeks. Solid-phase chemical and mineral characterization, and aqueous-phase (drainage quality) chemical analyses from these kinetic tests have been archived in 14 MN DNR contract reports. Summaries of the BLM-funded laboratory studies have been published in 2 peer-reviewed journal papers.

BLM sponsorship of the research since FY 1997 has enabled the University to increase the number of chemical species in the laboratory humidity-cell model from 28 to 57, and increase the chemical reactions from 21 to 48. Additionally, the laboratory model operates under both acid and alkaline conditions. Currently, the humidity-cell model has been calibrated with samples from 5 different waste-rock lithologies. Fifteen chemical reactions have been added to the field test-pile model since the beginning of FY1997, and of the 15 new reactions 7 have been mathematically tested.

BLM-supported University modeling progress has been summarized in 5 contract reports, 2 M.S. theses, and 3 peer-reviewed journal papers.

## **OBJECTIVES**

The initial objective of our research was to be able to predict drainage quality from metal-mine waste rock. However, because a variety of lithologies commonly comprise waste-rock dumps, we recognized that this prediction had to be made through conducting and mathematically modeling accelerated-weathering tests of individual waste-rock lithologies. This generated several additional objectives that included:

- Assessing laboratory-test methods used for classifying mine waste,
- Identifying problematic waste-rock lithologies by subjecting sample suites from selected lithologies to commonly used laboratory accelerated-weathering tests,
- Correlating resulting laboratory-test drainage quality with corresponding sample mineral- and chemical-characterization data,
- Conducting field tests of individual waste-rock lithologies to 1) determine field rates of chemical release, and 2) assess the efficacy of extrapolating laboratory drainage pH to that of field tests of the same lithology, and
- Generating mathematical models that provide predictive tools to help ensure environmentally sound management of mine waste on the public lands.

## METHODS

### Laboratory and Field Testing

#### *Laboratory Kinetic Tests*

#### Materials

The current study includes 63 waste-rock samples that comprise eight lithologies. Twenty-one of the 63 samples were from a single lithology, siltite-argillite rock. The other 42 rock samples were from the remaining seven waste-rock lithologies: Duluth Complex gabbro (1), mafic-intrusive (7), tuffaceous-sedimentary (9), weathered carbonate-hosted, base-metal-sulfide bearing waste rock from a 75- to 100-year old oxidized metal-mine waste-rock dump (1), Archean greenstone (14), syenite porphyry (4), and selenium-bearing rhyolite (6).

The siltite-argillite samples were collected from blast-hole drill-cuttings, bulk samples, and from a bench surface at an open pit mine (Lapakko 1998a). The Duluth Complex gabbro rock was collected from a test pile that had been exposed to weathering for 15 years (Lapakko 1994, Eger and Lapakko 1985). The mafic-intrusive and three tuffaceous-sedimentary rocks, were segregated from a “sulfide-carbonate mixed waste” bulk sample from an open-pit metal mine; six additional low neutralization potential tuffaceous sedimentary rocks were collected from the same mine (Lapakko and others 2002a). The weathered waste rock sample is a carbonate-hosted, base-metal-sulfide bearing waste rock from a 75- to 100-year old oxidized metal-mine waste rock dump, and was provided by Kathleen Smith of the U.S. Geological Survey (USGS) (Lapakko and others 2002a). This sample is referred to as the USGS abandoned mine land waste rock sample (USGS AML). The Archean greenstone samples were collected from core drilled in preparation for constructing a cavern for purposes unrelated to mining (Lapakko and others 2002b). The syenite porphyry samples were collected from a bench surface and its exposed highwall at an open-pit metal mine (Guard 1997). Bulk samples of selenium-bearing rhyolite samples were collected from two different hydrothermal-alteration zones at an open-pit metal mine (Trujillo and others 2000).

#### Procedures

**ASTM Method D 5744-96 (Accelerated Weathering “Modified-Humidity Cell” Protocol)** - A 16-cell array identical to that illustrated in the standard method was used (ASTM 2000, Figure 2, p. 262). This accelerated weathering test method is designed to increase the geological-chemical-weathering rate for selected 1000-g solid material samples and produce a weekly effluent that can be characterized for dissolved weathering products. This test method is performed on each sample in a cylindrical cell. Multiple cells can be arranged in parallel; this configuration permits the simultaneous testing of different solid material samples. The test procedure calls for weekly cycles comprised of three days of dry air (less than 10% relative humidity) and three days of water-saturated air (approximately 95% relative humidity) pumped up through the sample, followed by a leach with water on Day 7 (ASTM 2000, pp. 257-269; White and Lapakko 2000).

**MN DNR Method** - A kinetic test method similar to ASTM Method D 5744-96 was designated as the MN DNR method. The MN DNR method uses the same humidity-cell diameter, waste-rock charge, and rinse volume and application method as described in the ASTM method D 5744-96, section 6.1 (ASTM 2000, p. 259). The MN DNR cell was about 3 cm shorter than the ASTM cell. The latter had a thicker base plate; a larger space, to accommodate a fitting for introducing air flow, between the base plate and perforated plastic support; and a thicker cover. As was the case for the ASTM method used in this project, a week-0 rinse volume of 1.5 L is used rather than the 0.5 L volume described in the standard method (0.5 L was used in all succeeding rinses). However, instead of subjecting the humidity cell apparatus to the humid or dry air flow into the cell, the cells were stored in a controlled temperature and humidity room between weekly rinses. It should be noted that the relative humidity readings were from the room itself. The humidity within the cells was probably near 100%, since the water retained in the cells was fairly constant during the weekly cycles (i.e. water did not evaporate).

**ASTM and MN DNR Rinse Alternatives** - Two cells, one ASTM and one MN DNR, containing Duluth Complex gabbro rock were also run to examine the effect of using a “flood” rinse rather than the “drip-trickle” rinse described in the standard method. During the flood rinse, water was dripped into the cell (to avoid disturbing the solids) from the separatory funnel until about two cm of water accumulated above the rock. Water was then added in a steady stream. The 500-mL rinse volume was used in all tests.

### ***Greenstone Field Test Piles***

Four 50 cubic yard piles (63 metric tons) were constructed to examine the dissolution of greenstone rock under field conditions (Figure 1).

Dimensions of the piles were the same, with bases 20 feet square, tops eight feet square, and a height of six feet. The rock was analyzed for particle size distribution and chemistry, and mineralogical analyses are planned. The sulfur contents of the four piles were 0.02, 0.20, 0.39 and 0.67 percent.

Precipitation at the site was measured using a US Standard rain gage. Precipitation falling on the piles, passed through the rock and an underlying sand layer (six inches), and flowed along a 36 mil reinforced polypropylene (RPP) liner to a slotted PVC collection pipe. The drainage then flowed to a sump equipped with a pump activated by the water level in the sump. Sump discharge passed through a flow meter, after which a sample was automatically deposited in a collection bottle for subsequent analysis for pH, alkalinity/acidity, sulfate, and major and minor cations. The piles were also equipped with instrumentation to determine temperature and oxygen



**Figure 1. - MN DNR field test piles of Archean Greestone rock.**

concentrations within the pile at the bottom of the pile and at a height of three feet above the bottom.

## ***Analyses***

### **Solid Phase**

Particle size distributions of the mine waste samples were determined by Lerch Brothers, Inc., Hibbing, MN. The mine waste samples were analyzed for sulfur, sulfide, sulfate, evolved carbon dioxide, as well as whole rock and trace constituent concentrations by ACTLABS, Inc., Tucson, AZ. Analyses to determine mineralogic composition and degree of liberation of sulfide and carbonate minerals were conducted on selected siltite-argillite samples (Lapakko 1998a) and the mafic-intrusive, tuffaceous-sedimentary, and USGS AML samples (Lapakko 1999c). These analyses were conducted using x-ray diffraction, optical microscopy, and SEM by Barry Frey of Midland Research (Nashwauk, MN) and Louis Mattson, Mineralogical Consulting Service (Pengilly, MN). Mineral content of the greenstone samples was determined by Louis Mattson using sample chemistry, optical microscopy, and previous x-ray diffraction data on drill core samples.

### **Aqueous Phase**

Water samples were analyzed for specific conductance, pH, alkalinity, acidity, and Eh at the MN DNR in Hibbing. Specific conductance was analyzed using a Myron L conductivity meter, and an Orion SA720 meter, equipped with a Ross combination pH electrode (8165), was used for pH analyses. Alkalinity (for pH  $\geq$  6.3) and acidity were determined using standard titration techniques for endpoints of 4.5 and 8.3, respectively (APHA and others. 1992). Eh readings were taken using a Beckman model 11 meter with an Orion electrode (9678BN).

Prior to 23 August 1999, metals were determined with a Varian 400 SPECTRAA; a Zeeman GFAA furnace was attached for low concentrations. Subsequent analyses were conducted using inductively coupled plasma mass spectrometry (ICP-MS, Hewlett Packard HP4500 Series, model #G1820A). Sulfate concentrations exceeding five mg/L were determined using a Technicon AA2 automated colorimeter. Lower concentrations were determined using a Dionex ion chromatograph and, after 10 November 1998, a Lachat QuickChem 8000.

### **Mathematical Modeling**

#### ***Rationale***

The overall objective of the joint research was to be able to predict water quality from metal-mine waste by developing predictive tools that would help ensure environmentally sound management of mine waste on public lands. To accomplish this objective, the developing mathematical-predictive model needed to be:

- Based on robust scientific foundation,
- Calibrated with long-term laboratory accelerated-weathering test data, and

- Supported by laboratory tests performed on multiple mine-waste lithologies

Accelerated weathering in humidity cells has been a laboratory-test method commonly used in the U.S. and Canada to estimate drainage quality from mine-waste samples (Bradham and Caruccio 1991; Ferguson and Morin 1991; White and Jeffers 1994). Because of the method's widespread use, we wanted to determine if it was possible to mathematically model the weekly drainage chemistry resulting from this laboratory test. While conditions common to humidity-cell kinetic tests differ from those encountered in actual waste-rock dumps, reaction-controlling conditions within each cell can be fixed at predefined limits. Humidity-cell experiments (1) are essentially isothermal, (2) have an ample supply of oxygen, and (3) are characterized by well-defined gas-transport and water-flow systems. These conditions not only accelerate the weathering process but also have potential to identify rate-limiting steps characteristic of both chemical and physical processes that occur with oxygen in abundance (White and others 1994). Therefore, the modified humidity-cell protocol was selected as the laboratory method to model.

Our objective in successfully modeling drainage quality from humidity cells was to 1) identify the controlling geochemical reactions responsible for generation and neutralization of contaminated drainage from a variety of mine-waste lithologies, and 2) use these controlling reactions to develop a more complex three-dimensional model that could simulate drainage quality from a waste-rock dump composed of metal-mine waste under more realistic environmental conditions.

To provide empirical data to the USBM for the modeling effort, modified humidity-cell tests were conducted by USBM from 1991 through 1995 on two different mine-waste lithologies. The consequent protocol refinement and resulting empirical data were the basis for identifying the controlling geochemical reactions used in the mathematical modeling. By the time USBM was closed in early 1996, two kinetic models had been developed, a laboratory humidity-cell model, and a field test-pile model. Since 1996, humidity-cell testing of six additional lithologies and the consequent improvement of both kinetic models has been continued by MN DNR and the University under BLM sponsorship. The following sections describe the first principles of each model and the evolution of their respective development.

### ***Laboratory Conceptual Model***

#### **Description**

The University, which was under contract to the USBM from 1992 through 1995, designed a preliminary model that simulated chemical changes that occur in the weekly interstitial water remaining in each humidity cell (Lin 1996; White and Jeffers 1994; White and others 1994). Rather than solve the customary diffusion and convective-transport equations for a packed column of reacting particles, a different approach was taken. The humidity cell was conceptualized as 20 continuous-stirred tank reactors (CSTR's) in series. Twenty CSTR's were used because this number approached the same effluent results as a packed-bed model with axial dispersion.

As of 1994, the model used 10 simultaneous chemical reactions and 14 different chemical species to describe the generation and neutralization of acid in the humidity cell. Solid species

included pyrite, calcium carbonate, ferric hydroxide, jarosite, and feldspar. Aqueous species included sulfate, ferrous and ferric ion, oxygen, calcium, potassium, carbonate ion, and hydrogen ion (pH). Bacterial catalysis of acid production was modeled using a modified Monod-type relationship for the growth phase that accounted for pH dependency and included a term that accounted for the death phase. The weekly cycle of leaching with 500 mL of de-ionized water (1 day), pumping dry air (3 days) and then water-saturated air (3 days) was modeled, taking into account the volume change in interstitial water and the resulting evaporation.

Because air is pumped continuously through each humidity cell at 1.0 L/min for both the wet- and dry-air cycles, the concentration of oxygen in the interstitial water was assumed to be constant at saturated conditions during this time period. During the leaching step, however, air is not being pumped and oxygen in the aqueous phase was allowed to decrease in accordance with its consumption for the designated chemical reactions. The solid-phase reactions include the effects of oxygen diffusion through the reacted portion of the particles.

The kinetic constants in the model were assumed to be fixed and dependent only on temperature, which was not considered to be a variable in these experiments. Kinetic constants were obtained by comparing the experimental effluent compositions collected during the water-leaching phase of the weekly cycle with those predicted by the model (Lin 1996; White and others 1994).

### **Basic Model Components**

Two commonly-used chemical models comprise the University's conceptual laboratory humidity-cell based model, and are considered to be operating simultaneously:

- Shrinking core model - describes the solid-liquid reaction of rock particles with interstitial water remaining in the mine-waste sample during and after each weekly leach.
- Continuous-Stirred Tank Reactor (CSTR) model - 1) describes the mixing and reaction of dissolved and undissolved components in water as a whole, and 2) when used in a series of reactors, describes the transport and resultant concentration gradient from top to bottom of the waste rock sample in the humidity cell as a result of each weekly 500-mL leach.

### **General Assumptions**

Rock particles in the sample are assumed to be uniform and spherical and have a constant porosity. Each rock particle is considered a composite of all the minerals comprising the mine-waste sample. Rock particles and interstitial water remaining after the leach are simulated to be well mixed in the series of CSTRs. Initial composition of the interstitial water in all CSTRs is assumed to be the same as the first recovered leach composition.

During the 6 days of the weekly cycle following the 2-hour leach, it is assumed that sample rock particles react with the new interstitial water according to the shrinking-core model, and the rock particles and interstitial water are well mixed according to the CSTR model. Based on experimental data collected by USBM, the pore-water volume remaining after the leach decreases with time during the 3-day dry air step. Evaporation reduces the post leach interstitial-water volume

by about one half, which causes an increase in the dissolved species concentrations. This is accounted for in the model by the mass balance equations that describe the aqueous species concentrations in the stacked CSTRs during the dry-air step (Lin 1996).

### ***Evolution of the Laboratory Model***

Since all mathematical models are simulations of the actual event under a given set of assumptions, the model must be compared to experimental data in order for verification. To develop and calibrate the humidity-cell based laboratory model, modeled output was compared with weekly drainage-quality data from long-term humidity-cell tests of waste-rock samples. Weekly drainage-quality data included pH, specific conductance, and major ion and trace-metal concentrations (e.g., iron, sulfate, calcium, magnesium, arsenic, copper, selenium, uranium, and zinc). Eight different waste-rock lithologies were subjected to humidity-cell tests during the 1991 - 2002 period and modifications were made to the humidity cell model during this same time period. The period of record for these humidity-cell tests ranged from 20 to 247 weeks (Table 1).

Table 1. - Summary of eight waste-rock lithologies subjected to humidity-cell tests from 1991 to 2002.

| Lithology              | Number of Samples | Period of Record, Weeks |
|------------------------|-------------------|-------------------------|
| <b>1991-1995:</b>      |                   |                         |
| Siltite Argillite      | 2                 | 218                     |
| Duluth Complex         | 8                 | 60-137                  |
| <b>1996-2002:</b>      |                   |                         |
| Siltite Argillite      | 21                | 20-278                  |
| Mafic Intrusive        | 7                 | 102-168                 |
| Tuffaceous Sedimentary | 9                 | 20-168                  |
| Duluth Complex         | 1                 | 265                     |
| USGS AML               | 1                 | 158                     |
| Archean Greenstone     | 14                | 100                     |
| Syenite Porphyry       | 4                 | 32                      |
| Se-bearing Rhyolite    | 6                 | 52                      |

To date, modeled output has been compared with weekly drainage quality from humidity-cell testing of samples of siltite-argillite, Duluth-Complex, syenite-porphyry, and Se-bearing Rhyolite lithologies (Lin 1996; Guard 1997; Trujillo and others 2000; White and others 1994).

The model was also recently used to simulate drainage quality from a pyritic quartz-carbonate

tailings sample that had been subjected to 520 weeks of laboratory accelerated-weathering tests, and whose actual drainage quality transitioned dramatically from neutral to acid pH. Our objective was to see if the model could also predict a similar pH transition. The laboratory data are from a tailings sample comprised of relatively uniform, small particle size and well-liberated minerals. Input to the model was based on converting the tailings' particle size distribution to an average particle diameter and using the same amount and configuration as a waste rock sample (i.e. 1000 g). Since not all minerals are represented in the model some approximations had to be made. Table 2 shows the comparison between actual tailings parameters and simulated waste-rock parameters for the quartz-carbonate tailings sample T9.

Although arsenopyrite is included in the current model, it was not used to simulate these samples. Sphalerite was also not included in the model since it was not present in a significant amount. The other minerals, from barite to apatite, are not included in the model. Quartz is considered to be an inert mineral in the present version of the model and is a good approximation as long as the pH does not fall below 2.0 or so and the temperature is low. Thus, in order to bring the total percentage up to approximately 100 percent, the other minerals are combined into the quartz value for the model input. This procedure isn't really necessary but serves as check to make sure all components of the sample are accounted for in one way or another.

Table 2. - Mineralogical data for quartz-carbonate tailings sample T9, and corresponding model input values

| Mineral      | T9, Weight Percent |             |
|--------------|--------------------|-------------|
|              | Experimental Data  | Model Input |
| Pyrite       | 6.57               | 6.57        |
| Pyrrhotite   | 0.13               | 0.13        |
| Chalcopyrite | 0.01               | 0.01        |
| Calcite      | 1.4                | 1.4         |
| Siderite     | ND                 | 0.1         |
| Feldspar     | 27.6               | 27.6        |
| Olivine      | -                  | 1.0         |
| Quartz       | 27.5               | 63.3        |
| Barite       | 14.22              |             |
| Arsenopyrite | 0.05               |             |
| Molybdenite  | 0.19               |             |
| Galena       | <0.01              |             |
| Stibnite     | 0.04               |             |
| Sphalerite   | 0.02               |             |
| Dolomite     | ND                 |             |
| Ankerite     | <0.3               |             |
| Mica         | 16.2               |             |
| Chlorite     | 2.1                |             |
| Amphibole    | 2.9                |             |
| Magnetite    | <0.1               |             |
| Apatite      | <0.3               |             |

Because the major mineral constituents comprising each sample were the primary input to the laboratory model, mineral weathering reactions and their associated rate laws were gradually added to the model over time. During 1991-1995, abiotic and biotic iron-sulfide mineral oxidation and consequent acid production were the initial reactions incorporated into the model. Carbonate- and

silicate-mineral acid neutralization reactions, and secondary mineral precipitation reactions (i.e., jarosite, gypsum, and iron hydroxide) were also included during this period (Lin 1996; Trujillo and others 1994; Trujillo and others 1996a; White and Jeffers 1994; White and others 1994).

The additional metallic-mineral weathering reactions for zinc and uranium were added in 1996-1997 (Guard 1997; Trujillo and others 1996b). Because the initial model was confined to simulate acid conditions, and contaminated drainage includes mobilization of arsenic, selenium and uranium oxyanions under alkaline conditions, the model was modified to simulate both acid and alkaline conditions during 1996-2000. Arsenic- and selenium-mineral weathering reactions were also incorporated into the model during this time (Trujillo and others 1998; Trujillo and others 2000). More recent changes have included adding siderite as a shrinking core species that can act as a neutralizing mineral but releases ferrous ion as well. These modifications were developed by the University so that 1) drainage quality from a larger variety of waste-rock lithologies could be modeled, and 2) the model would be more robust and applicable to a wider range of waste-rock types under both acid and alkaline conditions.

### ***Field Conceptual Model***

#### **Description**

Prior to USBM's closure, five geochemical reactions selected from the 23-reaction suite identified during the 1995 humidity-cell modeling effort were used by the University to develop a three-dimensional, three-phase geochemical model that would describe the drainage quality from test piles of discrete rock types (i.e., individual lithologies) when exposed to actual field conditions. This effort was made in order to develop a more realistic model that could be used to predict drainage quality from field operations.

#### **Basic Model Components**

The rate laws and associated parameter values of these five governing-geochemical reactions were linked with equations that describe transport phenomena in porous media with three phases (i.e., mass, momentum, and energy balances for solid, liquid and vapor phases). The resulting equations were incorporated into a three-dimensional test-pile simulation. A truncated pyramid-shaped waste-rock test pile was computer simulated and assumed to be composed of a single rock type (lithology). The simulated test pile was represented by multiple layers, and each layer was comprised of multiple building blocks with block dimensions dictated by the size of the test pile and the number of blocks used. The number of blocks used is only limited by the computational resources available. Recent efforts have been made to run large block systems on the supercomputer at the University of Utah.

#### **General Assumptions**

Each building block was considered to be a uniform grid point where a specific rock composition and solid-liquid-phase permeabilities could be fixed, and the initial aqueous saturation levels, bacterial populations and oxygen concentrations could be varied. The governing geochemical

and transport equations were operative in each building block, and each block was linked to adjacent blocks. More details of the model can be found in the literature (Lin 1996; Lin and others 1997).

## **RESULTS AND DISCUSSION**

### **Laboratory and Field Testing**

#### ***Development of Kinetic Test Protocols***

##### **ASTM Method D 5744-96**

**Introduction** - A “modified humidity cell” kinetic-test protocol, incorporating the humidity cell design and weekly protocol by Lawrence (1990), was augmented by the U.S. Bureau of Mines (USBM) at its Salt Lake City Research Center. Based on this protocol, and using data generated by long-term USBM humidity-cell tests (White and Jeffers 1994), a draft standard test method for the modified humidity cell was initiated in 1992 by USBM and the American Society for Testing and Materials (ASTM). The intent of the method’s authors was to provide in one readily accessible document (i.e., the Annual Book of ASTM Standards, v. 11.04) a more detailed description of the modified humidity cell protocol than was previously available in the literature. The ultimate goal of the authors was to promote method consistency and provide a helpful guide to new users of the modified humidity-cell protocol, not to impose a prescriptive protocol upon the acid-mine drainage research and practitioner community. Subjecting various rock types to a well-defined standard test makes results more useful, since data can be more readily compared, interpreted and extrapolated. One effort on compiling kinetic test data is presently in progress (Morin and Hutt 1999; Morin and others 1996).

**ASTM Method Approval Process** - Creating a standard method through ASTM is a consensus process that involves multiple steps. Eight drafts of the modified humidity cell protocol were peer reviewed by ASTM task group, subcommittee, main committee, Society, and editorial staff members during a four-year period. Also during this period, more advanced versions of the draft method were reviewed by several members of U.S. state and federal regulatory agencies, as well as selected Canadian and U. S. researchers of contaminated drainage from metal-mine wastes. The ASTM consensus process designated the augmented protocol as ASTM Method D 5744-96 in March 1996 (ASTM 2000).

An ASTM requirement for standardizing test methods includes the determination of intralaboratory (repeatability) and interlaboratory (reproducibility) replication of test results. This determination of precision is best accomplished through an interlaboratory study (ILS). At the time D 5744-96 was accepted as an ASTM standard method, it contained a preliminary precision statement based on intralaboratory replication from two different samples tested by USBM in duplicate humidity cells. To make the ASTM Method D 5744-96 precision statement more robust, an ILS was initiated in 1996 by the Bureau of Land Management (BLM continued the USBM's metal-mine waste studies after the 1996 closure of USBM).

An ILS is usually conducted by no fewer than six laboratories, and performed on at least three materials representing different test levels. After closure of USBM, only two laboratories (American

Assay Labs - AAL, and Minnesota Department of Natural Resources - MN DNR) were available to participate in a long-term study of the method (i.e. test duration \$ 20 weeks). Therefore, comparisons of humidity-cell data generated from waste-rock samples duplicated by these two laboratories were used to present preliminary indications of the method's repeatability and reproducibility. Whereas this study was unable to involve the number of laboratories prescribed by a formal ILS, it does provide a substantial amount of information on kinetic test replication, an area that has been recognized as lacking quantitative description (Mills 1999).

### ***Assessment of Test Methods***

The present study 1) assessed the repeatability and reproducibility of the ASTM method; 2) assessed the repeatability of the MN DNR method; 3) compared results from “flood” rinse alternatives to the standard “drip” rinse approach for the two methods; and 4) compared results from the ASTM method and the MN DNR method. It was recognized that replication of results for a given kinetic test method and comparative results between methods could vary with rock type. Consequently, a repeatability- and reproducibility-testing program was initiated using six of the eight waste-rock lithologies studied so far (siltite-argillite, Duluth Complex, mafic intrusive, tuffaceous sedimentary, Archean Greenstone, and USGS AML). However, not all six lithologies were used for every evaluation. Comparisons were usually based on drainage pH and rates of sulfate, calcium, and magnesium release over time, although in some cases were limited to drainage pH and sulfate release rate (Lapakko 1998b, 1999b; Lapakko and Antonson 2000c; Lapakko and White 2000; White and Lapakko 2000; Lapakko and others. 2002a, 2002b, 2002c).

Previous publications have used the terms “drip-trickle leach” and “flood leach” to describe the addition of water to the cells to remove reaction products. For this report “drip” is used in place of “drip-trickle.” This term describes the water addition and eliminates any presumption of describing, perhaps erroneously, the subsequent flow through the rock in the cell. The term “rinse” is used in place of “leach”.

The ASTM method drip and flood alternatives demonstrated very good repeatability (intralaboratory replication) and good reproducibility (interlaboratory replication). Reproducibility tended to decrease with test duration. Differences in reaction environment temperature among laboratories resulted in difference in rates of sulfate release, with sulfate release rates increasing with temperature. This dependence also produced cyclic variations in sulfate release rates with seasonal temperature variations within a laboratory. Results from the flood rinse alternative were not substantially different from those of the drip rinse alternative.

The MN DNR method drip alternative demonstrated very good repeatability and was not subjected to reproducibility evaluation. The flood alternative produced results similar to the drip alternative but was not tested for either repeatability or reproducibility.

The ASTM and MN DNR methods produced similar results with regard to classifying mine wastes for remediation purposes. That is, the relatively small differences observed in drainage pH values would not lead to different conclusions for mine waste management. Differences in magnesium release rates were attributed to differences in the amount of residual water in the cells during the weekly cycle. The ASTM method dry cycle tended to reduce the amount of residual water and, consequently, yield lower rates of magnesium mineral dissolution than the MN DNR method.

Furthermore, the amount of residual water in the ASTM method tended to vary more than in the MN DNR method.

Modifications to the ASTM method should be considered based on the data generated. Temperature apparently affected rates of sulfide mineral oxidation, and acceptable ranges should be established to increase test repeatability and reproducibility. The possible effects of variable and excess drying during the dry air cycle should also be considered.

## ***Dissolution of Waste Rock Lithologies***

### **Introduction**

The purpose of conducting dissolution tests on well-characterized solids is to determine relationship between solid-phase composition and drainage quality. This information will improve the accuracy of drainage quality prediction, increase the value of solid-phase compositional data for predicting drainage quality and reduce the time required for conducting kinetic tests. In summary, it will increase the accuracy and efficiency of generating data necessary to make decisions on the environmentally sound management of mine wastes.

This project examined dissolution as a function of solid-phase composition of siltite-argillite (Lapakko 1996, 1998a, 1999a, 2000), Duluth Complex gabbro (Lapakko 1996, 1998a, 1998b, 1999b; Lapakko and Antonson 2000b), mafic-intrusive, tuffaceous-sedimentary, weathered carbonate-hosted base metal sulfide (USGS AML) (Lapakko 1998c, 1999c; Lapakko and Antonson 2000a; Lapakko and others 2002a), and Archean greenstone (Lapakko and others 2002b) rocks. The project also considered previously generated data on laboratory and field dissolution of Duluth Complex gabbro (Lapakko 1988, 1994; Lapakko and Antonson 1994) and laboratory dissolution of quartz-carbonate tailings (Lapakko 1992; Lapakko and Wessels 1995).

### **USGS AML Rock**

The USGS abandoned mine land sample (AML) had a sulfide content of 13 percent and elevated concentrations of lead and zinc. The acid production potential associated with iron sulfide was calculated as 334 g CaCO<sub>3</sub> eq (kg rock)<sup>-1</sup>, and was calculated assuming all sulfide was associated with lead, zinc and iron. The CO<sub>2</sub> content of the sample was 20.9%. Calcium and magnesium present in siderite (52.1 weight percent of rock) and a small amount of calcite (0.2%) yielded a total NP[(Ca+Mg)CO<sub>3</sub>] of 55 g CaCO<sub>3</sub> eq (kg rock)<sup>-1</sup>. Substantial amounts of sphalerite (10%) and goethite (8%) were present. Minerals present at levels of 1 to 3 percent include melanterite, quartz, kaolinite, galena, and gypsum.

Drainage quality data indicated that the dissolution of carbonate minerals in the USGS AML sample was adequate to neutralize the acid produced by iron sulfide mineral oxidation. Drainage pH increased from values near 6.7 in the initial rinse to about 7.9 at about week 80 then typically remained in the range of 7.8 to 8.0 through the 158-week period of record. Elevated concentrations of alkalinity, magnesium and, to a lesser extent, calcium indicated magnesium and calcium carbonates were responsible for acid neutralization. The magnesium and calcium release further indicated that roughly 30% of the NP[(Ca+Mg)CO<sub>3</sub>] has been depleted. The estimated times to depletion range

from 0 to 450 weeks (respectively calculating availability using only liberated carbonates or total carbonates).

It should be noted that if management decisions for proposed or abandoned mine wastes were based on the existing drainage pH data (which is well within limits often required for discharges), potentially acid-producing mine waste could be erroneously classified. The abandoned mine waste sample did not produce acidic drainage during the dissolution test, and it is likely that the drainage from this rock in the field was neutral for 75 to 100 years. Based on its field behavior alone, rigorous remediation measures would probably not be prescribed. However, its Net NP was -280 g CaCO<sub>3</sub> equivalent (kg rock)<sup>-1</sup> [Net NP = NP[(Ca+Mg)CO<sub>3</sub>] - AP(FeS)], suggesting that the rock has a high potential to produce acidic drainage for decades. Thus, in the absence of characterization and long-term predictive testing, a mine waste which could adversely impact drainage quality might be left unremediated, while financial resources were expended toward reclaiming less reactive mine wastes.

### **Other High-Carbonate Iron Sulfide-Bearing Rocks**

As indicated by the USGS AML sample, rocks with even small percentages of calcium and magnesium carbonate minerals may produce neutral drainage for an extended period. After these long “lag times” the samples can produce acidic drainage. For example, hydrothermal quartz-carbonate gold tailings containing 1.4% calcite produced drainage pH values above 6.0 for 122 weeks. At this time values decreased below 6.0 and reached a minimum of 2.94 after 220 weeks (Lapakko and Wessels 1995).

For samples containing even moderate amounts of calcium and magnesium carbonate minerals, the potentially long “lag times” require kinetic tests of extended duration to empirically simulate field drainage over the long term. Drainage pH will remain circumneutral as long as acid neutralizing minerals are available for reaction and dissolve at a rate greater than or equal to the rate of acid production. A critical question regarding these mine wastes is the amount of acid producing and acid neutralizing minerals that will be available to react, as opposed to the total amount of these minerals present.

Three of the lithologies tested in the present project have provided initial preliminary data on the availability of calcium and magnesium carbonate minerals to dissolve and maintain drainage pH of at least 6.0. This availability was determined by continuing dissolution tests until drainage pH decreased below pH 6.0 and determining the amount of calcium and magnesium carbonates dissolved at this time. In addition to the USGS AML sample, three siltite-argillite, four tuffaceous-sedimentary, and seven mafic-intrusive rocks contained substantial amount of calcium and magnesium carbonate minerals in addition to iron sulfides.

Using the ASTM D5744-96 method, 24% of the neutralization potential present as calcium and magnesium carbonate (NP[(Ca+Mg)CO<sub>3</sub>]) in a siltite-argillite sample dissolved to maintain drainage pH above 6.0. This sample had an initial NP[(Ca+Mg)CO<sub>3</sub>] of 28 g CaCO<sub>3</sub> eq/kg and its drainage pH decreased below 6.0 after 25 weeks. Using the MN DNR method 31% of the NP[(Ca+Mg)CO<sub>3</sub>] present in a tuffaceous-sedimentary rock dissolved to maintain drainage pH above 6.0. This sample had an initial NP[(Ca+Mg)CO<sub>3</sub>] of 19 g CaCO<sub>3</sub> eq/kg and its drainage pH decreased below 6.0 after 20 weeks. The pH of drainage from one of the mafic-intrusive samples tested recently decreased below 6.0 and testing is continuing to determine if it will remain below 6.0. The initial

NP[(Ca+Mg)CO<sub>3</sub>] of this sample was 42 g CaCO<sub>3</sub> eq (kg rock)<sup>-1</sup> and drainage pH decreased below 6.0 after 204 weeks of testing. Preliminary estimates suggest approximately 60% of the NP[(Ca+Mg)CO<sub>3</sub>] was available to dissolve and maintain drainage pH above 6.0. It is clear that the fraction of initial NP[(Ca+Mg)CO<sub>3</sub>] that is “environmentally effective” varies among lithologies. Additional solid-phase examination of carbonate phases in fresh and leached solids has been initiated to determine variables controlling this fraction.

### **Low-Carbonate Iron Sulfide-Bearing Rocks**

The calcium and magnesium carbonate contents were very low in the Duluth Complex gabbro and Archean greenstone rocks examined. Consequently, silicate mineral dissolution played a major acid-neutralizing role in these rocks. Since these minerals neutralize acid much slower than carbonate minerals, acid conditions were generated sooner than in rocks containing substantial amounts of calcium and magnesium carbonates. The pH of drainage from both rock types tended to decrease with increasing sulfur content and dissolution time. With both the Duluth Complex rock and Archean Greenstone rocks tested, the laboratory data generated to date are adequate to provide guidance for environmentally sound mine-waste management decisions.

**Duluth Complex Rock** - At the MN DNR 16 samples of ground Duluth Complex rock (0.053 < d # 0.149 mm, 0.18% #S # 3.12%) were subjected to dissolution testing (Lapakko and Antonson 1994). Sulfur present in the rock occurs largely as pyrrhotite and the major host rock minerals are plagioclase, olivine and pyroxenes. Periods of record reported ranged from 69 to 150 weeks and tests were continued, with present records as long as 700 weeks.

Drainage pH values decreased with increasing sulfur content during approximately the first 300 weeks of testing. Influence of test duration on this relationship is especially evident when comparing 300-week with 150-week results for the same suite of samples, as 300-week pH values were generally lower. Duluth Complex rock with sulfur contents less than or equal to 0.22% produced drainage pH values above 6.0 (Lapakko and Antonson 1994). The next highest sulfur contents tested were 0.40% and 0.41%. The former produced drainage pH values above 6.0 and the latter produced values below 4.5 (MN DNR unpublished data). Due to the uncertainty of the drainage quality from rock with sulfur contents near 0.4%, it can only be concluded that “critical sulfur content” for this Duluth Complex gabbro, below which drainage pH will be above 6.0 and above which drainage pH was less than 6.0, falls in the range of 0.22% to 0.4% sulfur. The MN DNR plans to test rock in this range and to more closely examine the influence of individual silicate minerals present in the Duluth Complex on acid neutralization.

Drainage pH values, and rates of sulfate, calcium, and magnesium release in the laboratory were compared to those generated by field test piles [830 to 1300 metric tons; 0.63% S (three piles), 0.79% S, 1.41% S] over 12 to 14 years (Lapakko and Antonson 1994). Field values for the 0.63% S pile were in close agreement with those observed for laboratory solids of similar sulfur content. Drainage pH values observed for the 0.79% S and 1.41% S were about one unit lower than those observed for laboratory solids of similar sulfur contents. Laboratory drainage pH values continued to decrease and approximated the field values for these two piles after 300 weeks of dissolution. Rates of sulfate, calcium, and magnesium release in the field were roughly 10 to 40 percent of those observed in the laboratory.

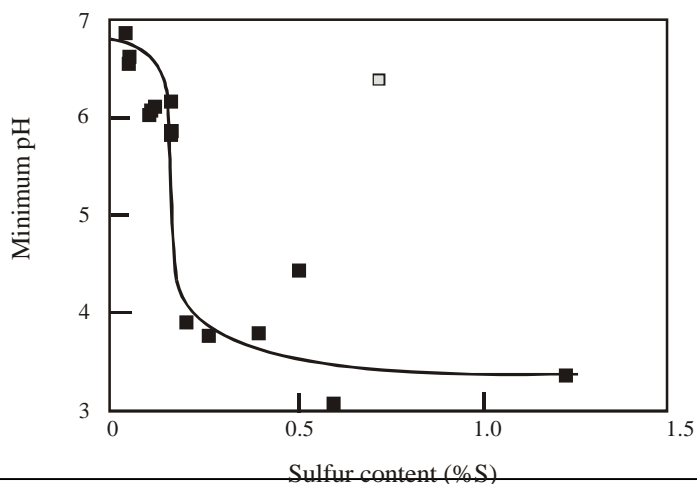
**Archean Greenstone Rock** - Fourteen samples of Archean greenstone rock were characterized (particle size, chemistry, mineralogy) and subjected to dissolution testing in the cooperative study between the US BLM and MN DNR (Lapakko and Antonson 2001, 2002; Lapakko and others 2002b). Sulfur content ranged from 0.04 to 1.22%, and occurred almost exclusively as pyrite. Major host rock minerals were quartz, chlorite, and sericite, and constituted 90 to 98 weight percent of the mineral content in 13 of the 14 samples. Substantial siderite (4.6 and 17.9 weight percent), containing magnesium and much lesser amounts of calcium, was present in two samples having sulfur contents of 0.50 and 0.72%.

During 100 weeks of dissolution testing, all but one of the samples with sulfur contents greater than or equal to 0.20% produced minimum drainage pH values less than 4.5. The single exception was a sample containing small amounts of magnesium and calcium carbonates. Two different samples with sulfur contents of 0.16% were tested. The minimum drainage pH values observed for the two samples were 5.83 and 6.15. This indicates that 0.16% S approximates a critical sulfur content for this rock, above which acidic drainage will be produced (Figure 2). Testing is continuing to determine, in part, if drainage pH values from the seven samples with S  $\geq$  0.16% will decrease.

If these values remain in an acceptable range, the greenstone rock sulfur content alone will provide a strong indicator of how wastes should be managed. For example, greenstone waste rock containing more than 0.16% sulfur would require greater precautions for mitigation of drainage quality. A safety factor would likely be applied to this value to account for potential errors in analysis and handling.

Additionally, chemical, petrologic and mineralogic data were combined to calculate the pyrite surface area exposed (Lapakko and Antonson 2002). These values were combined with sulfate release data to determine rates of pyrite oxidation. The values determined were in good agreement with published rates for the abiotic oxidation of pyrite by oxygen (Williamson and Rimstidt 1994).

Four greenstone field test piles operated for the first full season in 2001. The sulfur contents of these piles are 0.02%, 0.20%, 0.39%, and 0.67%. To date, the drainage from all piles has been in the neutral range. Sulfate concentrations in all drainages indicate the pyrite present is oxidizing. For samples of similar sulfide content, sulfate release rates observed during the first year of field testing were 5 to 50 percent of those in the laboratory. Elevated concentrations of alkalinity, calcium and magnesium in the drainages indicate calcium and magnesium carbonates were dissolving to neutralize the acid produced. Testing will continue to 1) determine if drainages will acidify, and 2) increase the period of record and consequently enlarge the field database for comparison with laboratory rates.



**Figure 2. - Laboratory Archean Greenstone samples showing decrease in drainage pH with increase in solid-phase sulfur content.**

## Mathematical Modeling

### *Laboratory (Humidity-Cell Based) Model*

#### Modeling Progress

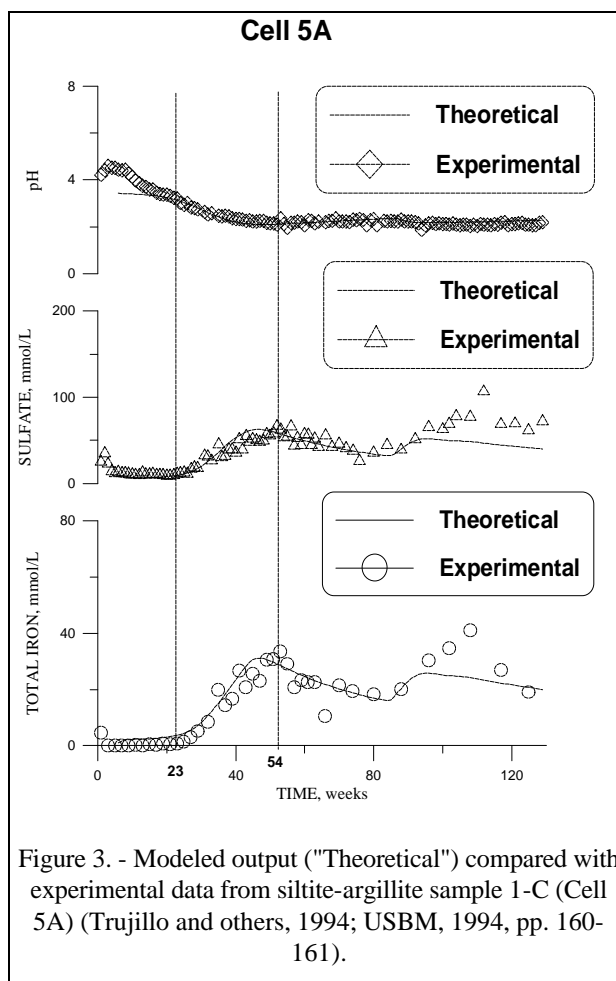
The University laboratory model AMDHC, v. 4.19 is now being used to predict weekly drainage chemistry from several samples of metal-mine waste rock that have been, or are currently being subjected to accelerated weathering in humidity cells (Trujillo and others 1994; Trujillo and others 1996a; Trujillo and others 1998).

Modeled weekly drainage chemistry exhibited good agreement with that of humidity-cell tests of samples from siltite-argillite (Lin 1996; Trujillo and others 1994; USBM 1994; White and others 1994) and hydrothermal quartz carbonate lithologies (see figures 4-6). As of FY 1995, the model duplicated three critical experimental responses observed in humidity-cell tests: 1) transition from abiotic to biotic iron-sulfide mineral oxidation; 2) precipitation of jarosite and concurrent reduction of total iron and sulfate concentrations because of precipitate coating of rock particles; and 3) participation and possible influence of two acidophilic bacterial populations on cyclic aqueous iron and sulfate concentrations (Figure 3).

There was also reasonable to fair agreement of modeled output with experimental drainage quality from Duluth Complex (USBM 1994), syenite-porphyry, and selenium-bearing rhyolite samples (Guard 1997; Trujillo and others 2000). However, additional kinetic testing of these lithologies is being conducted so that 1) the model can continue to be calibrated, and 2) the modeled fit to the experimental data can be improved.

#### Latest Modeling Results

The latest simulation has been conducted with the pyritic hydrothermal quartz-carbonate



tailings samples described earlier. Figures 4 and 5 show comparisons between experimental data and computer simulations for the T9 sample (mineralogy given in Table 2) for pH, sulfate and calcium. For this simulation only 14 of the 48 reactions were used and the constants for those reactions are given in Table 3.

Remarkably, the pH drop seen in the experimental data was also observed in the simulation (Figure 4).

According to the model, once calcite was depleted the pH reached a new level due to the neutralization by the feldspars and the siderite. Because the rate of neutralization by feldspars and siderite is less than that of calcite the pH dropped to a new level. The point at which that occurred depended primarily on the rate of oxidation of pyrite by oxygen and the rate of neutralization of the calcite. At the new level of pH, about 3.2 (3.7 in the model), the simulation indicated a gradual increase in the concentration of ferric ions, due to a gradual increase in bacteria concentration (catalyzing the conversion of ferrous ions to ferric). Eventually the ferric ion concentration reached a point where the oxidation of pyrite by ferric ions became important. At this point, the pH dropped even lower and then bacteria concentrations started to increase further, increasing the rate of

oxidation even further. This caused a sharp drop in pH and pyrite was quickly depleted. Once this happened, the pH started to rise since acid was no longer being generated. The rise in pH was much sharper in the model than experimental data indicate, perhaps due to adsorption/desorption or ion exchange effects not considered in the model. We are investigating this further.

The results for sulfate and calcium (Figure 5) also match experimental data fairly well for the same simulation. The maximum concentrations for both sulfate and calcium are occurring roughly at the same time as the experimental data but the peak concentrations for the simulation are considerably higher. This is consistent with the larger amount of material used for the simulation (1000 g versus 75 g). Experimentally, the total amount of sulfate and calcium released is consistent with all of the pyrite and calcite being depleted for the 75 g sample. Again, much sharper drops are observed in the simulation for sulfate and calcium than the data indicate, probably due to the reasons stated above for

Table 3. - AMDHC Version 4.19 Rate Constants – Hydrothermal quartz-carbonate tailings sample T9.

| <b>T9 – Modeling Run #463</b>                                    |                 |   |                         |
|--|-----------------|---|-------------------------|
| <b>Reaction</b>  | <b>Constant</b> | <b>Units</b>                                  |                         |
| (1) oxidation of pyrite by oxygen                                | KSO(1)          | L/cm <sup>2</sup> -s                          | 0.7 x 10 <sup>-11</sup> |
| (2) oxidation of ferrous ion                                     | KF(2)           | L <sup>3</sup> /mmol <sup>3</sup> -hr         | 3.0 x 10 <sup>-25</sup> |
| (4) oxidation of pyrite by ferric ion                            | KSF(1)          | L/cm <sup>2</sup> -s                          | 2.0 x 10 <sup>-10</sup> |
| (5) Calcite reaction with acid                                   | KSH(5)          | L/cm <sup>2</sup> -s                          | 2.0 x 10 <sup>-7</sup>  |
| (7) Bacterial growth and oxidation of ferrous ion                | MU1             | 1/hr  | 0.0190                  |
|  | KM7A            | mmol/L  | 1.0                     |
|  | KS1             | mmol/L  | 1.44                    |
|  | RMMAX           | 1/hr  | 5.0x10 <sup>-20</sup>   |
|  | POW             | no units                                      | 1.0                     |
|  | YXFE2           | mg-bacteria/mmol-Fe                           | 0.40                    |
| (8) Feldspar reaction with acid                                  | KSH(12)         | L/cm <sup>2</sup> -s                          | 1.0 x 10 <sup>-12</sup> |
| (9) Siderite reaction with acid                                  | KSH(29)         | L/cm <sup>2</sup> -s                          | 1.0 x 10 <sup>-11</sup> |
| (10) Formation of Jarosite                                       | KF(10)          | L <sup>0.667</sup> /mmol <sup>0.667</sup> -hr | 7.0 x 10 <sup>-15</sup> |
| (11) Oxidation of Chalcopyrite by Oxygen                         | KSO(16)         | L/cm <sup>2</sup> -s                          | 8.5x10 <sup>-13</sup>   |
| (12) Oxidation of Chalcopyrite by Ferric ion                     | KSF(16)         | L/cm <sup>2</sup> -s                          | 4.0x10 <sup>-13</sup>   |
| (14) Oxidation of Pyrrhotite by Oxygen                           | KSO(18)         | L/cm <sup>2</sup> -s                          | 7.0x10 <sup>-10</sup>   |
| (15) Oxidation of Pyrrhotite by Ferric ion                       | KSF(18)         | L/cm <sup>2</sup> -s                          | 5.0x10 <sup>-15</sup>   |
| (19) Bacteria II growth with jarosite, formation of ferrous ions | MMAX2           |   | 0.015                   |
|  | RMMAX2          |   | 0.001                   |
|  | POW2            | no units                                      | 2.0                     |
|  | YX2JA           | mg-bacteria/mmol-Fe                           | 0.5                     |
| (21) Reaction of Olivine with acid                               | KSH(27)         | L/cm <sup>2</sup> -s                          | 1.0x10 <sup>-13</sup>   |
| Diffusion Coef-O2  | D <sub>O2</sub> | m <sup>2</sup> /s                             | 1.0x10 <sup>-13</sup>   |
| Diffusion Coef-O2  | D <sub>Fe</sub> | m <sup>2</sup> /s                             | 1.0x10 <sup>-13</sup>   |
| Diffusion Coef-O2  | D <sub>H</sub>  | m <sup>2</sup> /s                             | 5.0x10 <sup>-13</sup>   |
| Avr. particle radius   | R               | cm  | 0.001800                |

pH.

It should be mentioned that this simulation is not unique, and other simulations could be obtained using slightly different rate constants and different mechanisms that also match experimental data. For example, a comparable match of the pH was also obtained when the jarosite rate was increased and the formation of jarosite caused the oxidation rate of pyrite to decrease almost to zero. Thus a rise in pH resulted at about the same time as the previous simulation, only this time pyrite was not exhausted (1000 g sample). More mineralogical data and postmortem analyses are needed to determine which simulation more accurately depicts the case for any given set of experimental data. Ongoing and future research will try to correlate the kinetic constants necessary to match experimental data for numerous lithologies to the mineralogy of the sample and other properties. If this is successful, then we should be able to predict what might happen in a standardized humidity cell test over a long period of time for any waste rock or tailings sample.

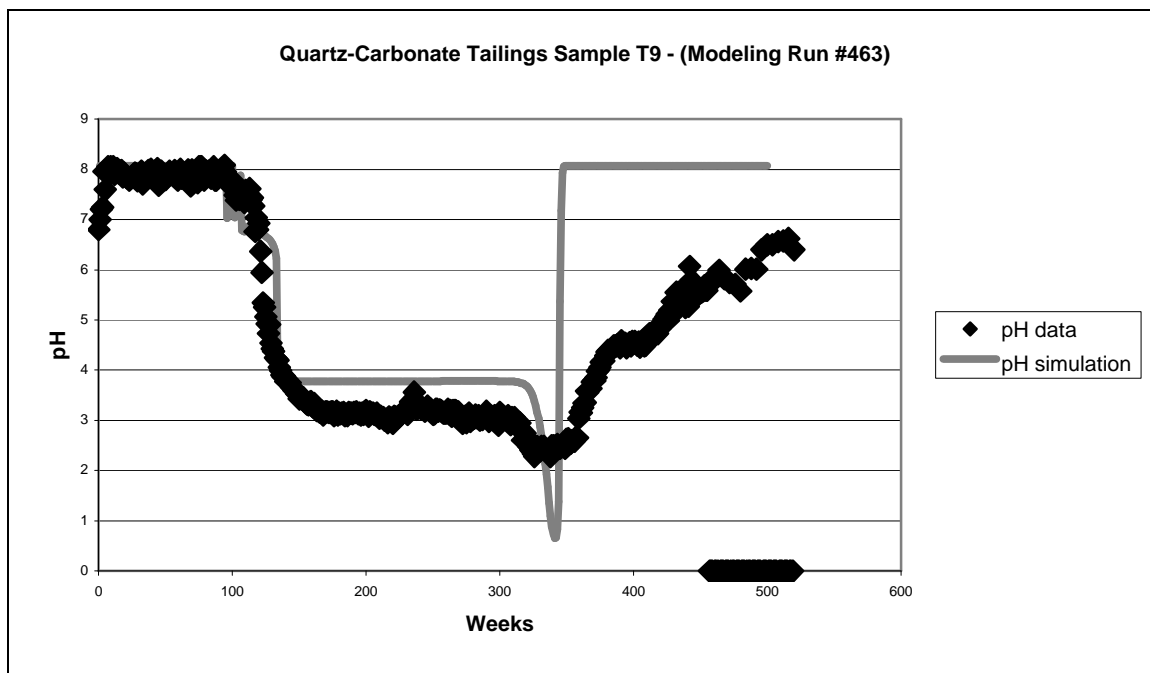


Figure 4. - Comparison between pH experimental data and computer simulation for sample T9.

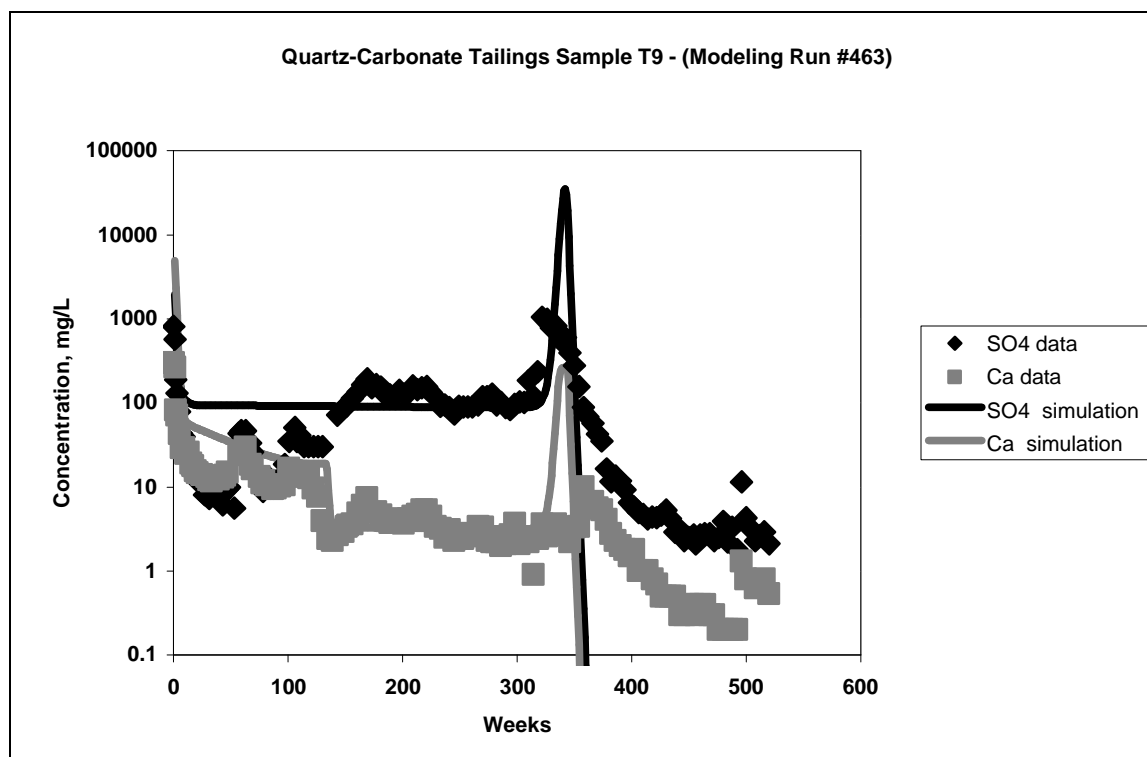


Figure 5. - Comparison between sulfate and calcium experimental data and computer simulation for sample T9.

Although the model is mathematically complex, access to the model is through a user-friendly PC-Windows NT/95/98 software program also developed by the University. Using this software program, the user is able to input data through a series of prompted pull-down "windows" and obtain an understandable output without being required to perform or derive complicated mathematical solutions. However, it has been found that in order to obtain excellent matches for widely varying lithologies, some adjustment of the kinetic constants is necessary and, in certain cases, only the most pertinent reactions should be included in the model. The following are examples of typical input and output:

- **Types of Data Required for Input:** Weight percent of certain minerals comprising the waste-rock type, estimate of initial bacterial concentration, average particle size, aqueous-phase concentrations from first week's humidity-cell drainage (both cationic and anionic), and desired number of weeks for the accelerated-weathering test are required.
- **Output:** Weekly plots of humidity-cell drainage pH, sulfate, iron (both ferrous and ferric), and specific ionic concentrations are provided in a series of Windows "boxes". Other available plots include bacteria concentrations and depletion of iron-sulfide and carbonate minerals.

The model software now contains 57 chemical species involved in 48 reactions and predicts the oxidation of pyrite, pyrrhotite, chalcopyrite, arsenopyrite, and uraninite. Also included are some selenium reactions and updated reactions for the carbonate system. The model has been modified to

accommodate drainage pH that is greater than 7 so it can model system drainages that are alkaline. The model currently simulates a maximum test duration of 500 weeks and creates concentration-versus-time plots for all 57 chemical species. Sixty-eight kinetic parameters are included in the current model for all 48 reactions. The magnitude of each kinetic parameter was initially established by applying trial and error curve-fitting techniques to the experimental data. Sensitivity analysis was then performed to assess the importance of each kinetic parameter on the modeled output. The resulting calculated parameters have been compared with corresponding kinetic parameters available in the literature when it was possible to do so and demonstrate reasonable agreement.

### ***Field (Test-Pile Based) Model***

During the initial mathematical testing of the test-pile model in 1995, it simultaneously solved more than 41,000 equations to produce concentration profiles for specified cross sections through the simulated test pile. Examples of symmetrical profiles that were calculated by the model include 1) oxygen in liquid phase, 2) pH, 3) water saturation, and 4) dump temperature (Lin and others 1997).

Since 1996, 15 more chemical reactions have been added to the original 5 reactions contained in the test-pile model. To date, 7 of the 20 reactions have been mathematically tested. It is possible to add more reactions to the field model so it eventually includes all of the 48 reactions contained in the laboratory humidity-cell model. However, computer-computation time increases substantially as the number of reactions are increased and some parameters in the modeled output become less stable (e.g., temperature oscillations have been observed). Before any future additions of reactions are considered, these two effects will need to be investigated. The computer code has been converted to use parallel processing and is now running on the University of Utah's supercomputer.

Recently, mathematical descriptions of lake phenomena (such as stratification, turnover, and other lake hydrodynamics) have been examined to see how they might be incorporated into the current test-pile model. Because the test-pile model links the governing geochemical reactions to transport phenomena in porous media, further linkage of the test-pile model with mathematical descriptions of lake phenomena may enable this multi-linked model to eventually predict metal-mine pit lake chemistry. Approximately 3 more years of research are needed to accomplish this mathematical linkage and initiate calibration with actual test data.

## **CONCLUSIONS**

Four main study areas were examined: 1) assessing laboratory kinetic-test methods, 2) classifying problematic waste-rock lithologies through use of laboratory accelerated-weathering tests, 3) conducting field tests of mine-waste lithologies to determine field rates of chemical release and compare laboratory with field drainage pH, and 4) generating mathematical models to predict drainage quality from waste rock to help ensure environmentally sound management of metal-mine waste. The following conclusions have been derived from these studies:

### **Assessing Laboratory Kinetic-Test Methods (ASTM and MN DNR Protocols)**

A standard accelerated-weathering protocol for mine waste associated with metal mining was established through ASTM's consensus-based process (ASTM Method D 5744-96), and a more

simplified protocol was established and tested by MN DNR (MN DNR Method). Additionally, both methods were subjected to rigorous intra- and interlaboratory studies to determine their repeatability and reproducibility with respect to variation in rinse application and pumped versus ambient air supply.

The ASTM method drip- and flood-rinse alternatives demonstrated very good repeatability and reproducibility. Results from the flood rinse alternative were not substantially different from those of the drip rinse alternative; however, reproducibility tended to decrease with test duration. Differences in reaction environment temperature were noted among laboratories, which resulted in different rates of sulfate release (sulfate release increased with increasing temperature). However, the difference in rates was cyclic, and these cyclic variations in sulfate release were correlative with seasonal temperature variation.

The MN DNR method drip-rinse alternative demonstrated very good repeatability, and the flood-rinse alternative produced similar results to those of the drip alternative. The ASTM and MN DNR methods produced similar results with regard to classifying mine wastes for remediation purposes; however, when compared with the MN DNR method, the ASTM method dry cycle tended to reduce the amount of residual water contained in the sample. This resulted in lower rates of magnesium dissolution and greater variability in interstitial water volume than was observed in samples subjected to the MN DNR method.

## **Classifying Problematic Waste-Rock Lithologies**

Mine waste characterization and drainage quality prediction are essential to environmentally sound management of abandoned mine wastes, as well as prior to mineral resource development. Drainage from mine wastes with substantial calcium and/or magnesium carbonate content can be neutral for decades and then acidify.

In the present project, an abandoned mine sample exposed to weathering in the field for 75 to 100 years was subjected to accelerated dissolution testing for 158 weeks in the laboratory. Although the sample produced neutral drainage in the field and laboratory, solid-phase analyses suggest the rock will eventually produce highly acidic drainage for an extended period of time. Clearly, in the absence of characterization and long-term predictive testing, a mine waste which could adversely impact drainage quality might be left unremediated, while financial resources were expended toward reclaiming less reactive mine wastes.

Estimation of drainage quality from mine wastes with even moderate amounts of calcium and/or magnesium carbonates based on solid-phase composition is difficult. Critical to prediction is the fraction of acid producing and acid neutralizing minerals that will be available to react, as opposed to the total amount of these minerals present. There is presently little published information quantifying this availability. The present study provided data on the availability of calcium and magnesium carbonates in siltite-argillite, mafic-intrusive, and tuffaceous-sedimentary rocks with neutralization potentials of 19 to 42 g  $\text{CaCO}_3$  equivalent  $(\text{kg rock})^{-1}$ . Drainage from these rocks acidified after 20 to 204 weeks and indicated availabilities of 24 to 60 percent. As the project continues, additional information on this availability will further improve the ability to estimate drainage quality based on solid-phase characterization.

Testing of two low-carbonate lithologies yielded data that provide strong guidance on which

to base mine waste management decisions. A critical sulfur range, below which rock produced neutral drainage and above which rock produced acidic drainage, was determined for both Duluth Complex rock and Archean greenstone rock. The critical sulfur range for the former was 0.2 to 0.4 percent and for the latter, 0.16 to 0.2 percent. Field drainage data, summarized below, for Duluth Complex rock support the laboratory data and similar field data are being generated for Archean greenstone rock.

### **Determining Field Rates of Chemical Release and Extrapolating Laboratory Drainage pH to that of Field Testing**

#### ***Duluth Complex Rock***

Drainage pH values, and rates of sulfate, calcium, and magnesium release in the laboratory were compared to those generated by field test piles. Field values were in close agreement with those observed for laboratory solids of similar sulfur content. Rates of sulfate, calcium, and magnesium release in the field were roughly 10 to 40 percent of those observed in the laboratory.

#### ***Archean Greenstone Rock***

Sulfate concentrations in the drainages from four greenstone field test piles indicate the pyrite present is oxidizing. Currently, drainage from all piles has been in the neutral range. For samples of similar sulfide content, sulfate release rates observed during the first year of field testing were 5 to 50 percent of those in the laboratory. Elevated concentrations of alkalinity, calcium and magnesium in the drainages indicate calcium and magnesium carbonates were dissolving to neutralize the acid produced. Testing will continue to determine if drainages will acidify, as implied by laboratory data, and to generate additional field data for comparison with laboratory rates.

### **Generating Mathematical Models to Predict Drainage Quality**

#### ***Laboratory (Humidity-Cell Based) Model***

As of FY 1995, the model (AMDHC) duplicated three critical experimental responses observed in humidity-cell tests: 1) transition from abiotic to biotic iron-sulfide mineral oxidation; 2) precipitation of jarosite and concurrent reduction of total iron and sulfate concentrations due to precipitate coating of rock particles and consequent reduction in iron-sulfide mineral oxidation rate; and 3) participation and possible influence of two acidophilic bacterial populations on cyclic aqueous iron and sulfate concentrations.

A recent application of the model (v. 4.19) to predict drainage chemistry from a hydrothermal quartz-carbonate tailings sample showed good to reasonable agreement with 520 weeks of experimental data including weekly drainage pH, and sulfate and calcium concentrations. The multiple drops in effluent pH were faithfully matched by the modeled output, and the model provided plausible explanation regarding the multiple drops and ultimate rise in pH. The same simulation

conditions showed that modeled results for sulfate and calcium also reasonably matched experimental data. These matches were obtained by limiting the modeled species to those contained in the sample (rather than having the model crunch through its entire inventory of reactions), and by making minimal changes to some selected kinetic rate constants. However, the simulation conditions that resulted in a reasonable modeled match to the quartz-carbonate experimental data were not unique. For example, when the rate of jarosite formation was increased, a comparable match of the pH was also obtained. Therefore, additional pre- and post-leaching mineral characterization is needed to identify which simulation conditions more accurately describe the actual mineralogical and physical conditions that produced the experimental data.

### ***Field (Test-Pile Based) Model***

The current version of the field model links governing geochemical reactions to transport phenomena in porous media. Consequently, the field model is able to produce concentration profiles for specified cross sections through a simulated symmetrical test pile. These concentration profiles include 1) oxygen in liquid phase, 2) pH, 3) water saturation, and 4) dump temperature. Further linkage of the test-pile model with mathematical descriptions of lake phenomena is being examined, and may enable this multi-linked model to eventually predict pit lake chemistry.

Although the number of reactions included in the model has been increased from the original 5 to 20, only 7 of these 20 reactions have been mathematically tested to date. Approximately 3 more years of research are needed to test the additional reactions, accomplish the lake-phenomena mathematical linkage, and initiate model calibration with actual test data.

## **CONSIDERATIONS FOR CONTINUED ASSESSMENT**

Considerable progress has been made towards 1) developing predictive tools (e.g. Guard 1997; Lapakko 1998b, 1999b; Lapakko and Antonson 2000b; Lapakko and others 2002c; Lapakko and White 2000; Lin and others 1999; Trujillo and others 1994; Trujillo and others 1996a; Trujillo and others 1998; Trujillo and others 2000; White and Lapakko 2000), 2) furthering the understanding of their application and interpretation (Lapakko 1993; Lapakko 1994; Lapakko and Antonson 2002; Trujillo and others 1997; White and others 1997, 1999), and 3) generating predictive data from long-term accelerated weathering tests of eight different waste-rock lithologies (Guard 1997; Lapakko 1996, 1998a, 1998b, 1998c, 1999a, 1999b, 1999c; Lapakko and Antonson 2000a; Lapakko and others 2002a, 2002b; Trujillo and others 2000).

Despite these advances, large gaps remain in the body of knowledge required for making scientifically based decisions on mine-waste management, and the following tasks need to be continued or expanded.

**Accelerated Weathering Tests** - Although eight waste-rock lithologies have been subjected to as much as 278 weeks of accelerated weathering in humidity cells, some of the samples have yet to be classified as either acid or non-acid producing. Therefore, selected samples should continue being subjected to accelerated weathering until their drainage quality can be determined. While these eight lithologies have been tested in this study, they are only a small representation of the numerous rock types that comprise metal-mine waste in the Western U. S. More waste-rock types need to be tested

to ensure that our study has examined a representative cross-section of metal-mine waste. The mineral- and chemical-characterization and accelerated-weathering data generated from testing additional rock types will help further the calibration of the two developing models so confidence is increased in the modeled output. The new data, along with data generated from previously tested waste-rock types need to be interpreted and organized into a comprehensive, diagnostic library of waste-rock drainage quality as a function of solid-phase composition. Additionally, several variables that influence rock dissolution in predictive tests (i.e., variation in rock composition, particle size, and pore-water retention time) have yet to be included in the accelerated-weathering-test protocol.

**Geochemical Predictive Models** - While the laboratory humidity-cell model is nearly complete, it needs to be further calibrated with additional waste-rock types to ensure that modeled output accurately reflects drainage quality from a broader range of waste-rock composition. The field test-pile model will require several years of additional work. Specifically, 13 of its current 20 geochemical reactions require mathematical testing, and additional mathematical testing will be required as more reactions are added. The model also requires calibration with actual test-pile data (MN DNR will provide 17 years of drainage-quality data from four 1000-ton test piles of Duluth Complex waste rock). To modify the field test-pile model to a pit-lake kinetic model, mathematical descriptions of lake phenomena will have to be linked to the model, which will require additional research effort and time. The field test-pile model is also capable of simulating 3-phase concentration profiles in large-scale laboratory column-leach tests and field heap-leach test piles. Further calibration of the model for these additional configurations is recommended.

Addressing these informational gaps and organizing and analyzing information collected in a systematic manner, are key elements of the proposed future work.

## ACKNOWLEDGMENTS

The authors gratefully acknowledge technical peer reviews that were conducted by the following: James F. Kohler, Chief, Branch of Solid Minerals, BLM Utah State Office, Salt Lake City, UT; Glenn A. Carpenter, Field Office Manager, BLM Salt Lake Field Office, Salt Lake City, UT (Management review); and staff members from Colorado Division of Mines and Geology, Denver, CO. Comments and suggestions from these peer reviews helped enhance the quality and organization of the report.

Humidity-cell testing at AAL was conducted under the supervision of Karl McCrea. John Folman, with assistance from Anne Jagunich and Patrick Geiselman, conducted humidity-cell testing at the MN DNR. James Baldwin, Ryan Cox, Margaret Finnegan, and Nathan Spencer conducted humidity-cell testing at the USBM Salt Lake City Research Center. University humidity-cell testing was performed by Freddy Guard, and Gautham Krishnamoorthy, and most of the University mathematical modeling was written by Cheng-Kuo Lin with assistance from Freddy Guard.

Funding for construction of the Archean Greenstone field test piles was provided by the MN DNR Division of Lands and Minerals. Funding for the remainder of the project was provided by the Minnesota Minerals Coordinating Committee and the Minnesota Environmental Cooperative Research Fund. MN DNR employees Tom Anderson, Al Dzuck, Pat Geiselman, Mike Lubotina, and Doug Rosnau assisted with construction of the field test piles. Andrea Johnson, with assistance from Doug Rosnau, was responsible for collection and analyses of field test-pile samples.

Charles Bucknam, Newmont Metallurgical Services, and Susan Sorini, Western Research Institute helped craft sections of ASTM standard method D 5744-96, and provided invaluable guidance during the interlaboratory studies of the ASTM and MN DNR humidity-cell protocols.

Since the closure of the U. S. Bureau of Mines (USBM) in early 1996, the original USBM metal-mine waste research has been continued under the generous sponsorship of the Bureau of Land Management (BLM). Without BLM's support, continuation of this study would not have been possible.

## REFERENCES

- Abandoned Mine Land Task Force. 1996. Abandoned mine land inventory and remediation: A status report to the Director, BLM. US Department of the Interior.
- American Public Health Association, American Water Works Association, Water Environment Federation. 1992. Standard Methods for the Examination of Water and Wastewater. 18<sup>th</sup> edition. American Public Health Association, Washington, DC.
- ASTM. 2000. D 5744-96, Standard test method for accelerated weathering of solid materials using a modified humidity cell. Annual Book of ASTM Standards, 11.04. American Society for Testing and Materials, West Conshohocken, PA. p. 257-269.
- Bradham, W. S., Caruccio, F. T. 1991. A comparative study of tailings analysis using acid/base accounting, cells, columns, and soxhlets. In Proceedings of the Second International Conference on the Abatement of Acidic Drainage. Montreal, Canada, September 16-18, 1991. p. 157-173.
- Eger, A.P., Lapakko, K.A. 1985. Heavy metals study. Progress report on the field leaching and reclamation study: 1977-1983. Minnesota Department of Natural Resources, Division of Minerals, St. Paul, MN. 53 p. plus appendices.
- Ferguson, K. D., Morin, K.A. 1991. The prediction of acid rock drainage - Lessons from the database. In Proceedings, Second International Conference on the Abatement of Acidic Drainage, Montreal, Quebec, September 16-18, Volume 3, p. 85-106.
- Guard, F. 1997. Humidity cell testing - an experimental and theoretical approach. U of UT Dept. of Chemical and Fuels Engineering, Master of Science Thesis, June 1997. 105.
- Lapakko, K.A. 1988. Prediction of acid mine drainage from Duluth Complex mining wastes in northeastern Minnesota. In Mine Drainage and Surface Mine Reclamation. V.1. Mine Water and Mine Waste. Proceedings of the 1988 Mine Drainage and Surface Mine Reclamation Conference. BuMines IC9183. p. 180-190.
- Lapakko, K. A. 1992. Characterization and static testing of ten gold mine tailings. In Proc. of 1992 American Society for Surface Mining and Reclamation Meeting. Duluth, MN, June 14-18, 1992. p. 109-119.
- Lapakko, K.A. 1993. Field dissolution of test piles of Duluth Complex rock. Report to the US Bureau of Mines Salt Lake City Research Center under Cooperative Agreement No. C0219003. 41 p. plus appendices.
- Lapakko, K.A. 1994. Comparison of Duluth Complex rock dissolution in the laboratory and field. In Proceedings of the International Land Reclamation and Mine Drainage Conference on the Abatement of Acidic Drainage, Pittsburgh, PA, April 24-29, 1994. p. 419-428.

- Lapakko, K.A. 1996. Laboratory drainage quality from siltite-argillite and Duluth Complex rock. Progress Report on Contract BLM J910P62009 to the U.S. Bureau of Land Management Salt Lake City Office, 27 November 1996. 12 p. plus appendices.
- Lapakko, K.A. 1998a. Laboratory drainage quality from siltite-argillite and Duluth Complex rock. Progress Report on Contract BLM J910P72015 to the U.S. Bureau of Land Management Salt Lake City Office, 11 February 1998. 41 p. plus appendices.
- Lapakko, K.A. 1998b. Laboratory drainage quality from Duluth Complex rock and assessment of test methods for waste rock dissolution. Final Report on Contract BLM JP910P72015 to the U.S. Bureau of Land Management Salt Lake City Office, 30 April 1998. 18 p. plus appendices.
- Lapakko, K.A. 1998c. Laboratory drainage quality from mafic-intrusive, tuffaceous-sedimentary, and weathered waste rocks. Progress Report on Contract J910C82009 to the U.S. Bureau of Land Management Salt Lake City Office, 30 November 1998. 20 p. plus appendices.
- Lapakko, K.A. 1999a. Laboratory drainage quality from siltite-argillite rock. Final appendices on Contract BLM J910C82009. 1 March 1999.
- Lapakko, K.A. 1999b. Laboratory drainage quality from Duluth Complex rock and assessment of test methods for waste rock dissolution. Report on Contract BLM J910C82009. 30 June 1999. 32 p. plus appendices.
- Lapakko, K.A. 1999c. Laboratory drainage quality from mafic-intrusive, tuffaceous-sedimentary, and weathered waste rocks. Progress Report on Contract J910C82009 to the U.S. Bureau of Land Management Salt Lake City Office, 30 June 1999. 34 p. plus appendices.
- Lapakko, K.A. 2000. Laboratory drainage quality from siltite-argillite rock. Final appendices on Contract BLM J910P82018. August 2000.
- Lapakko, K.A., Antonson, D.A. 1994. Oxidation of sulfide minerals present in Duluth Complex rock: A laboratory study. In Environmental Geochemistry of Sulfide Oxidation; ACS Symposium Series 550; American Chemical Society: Washington, DC, 1993. p. 593-607.
- Lapakko, K.A., Antonson, D.A. 2000a. Laboratory drainage quality from mafic-intrusive, tuffaceous-sedimentary, and weathered waste rocks. Final Report on Contract J910P82018 to the U.S. Bureau of Land Management Salt Lake City Office, 31 October 2000. 60 p. plus appendices.
- Lapakko, K.A., Antonson, D.A. 2000b. Laboratory drainage quality from Duluth Complex rock and assessment of test methods for waste rock dissolution. Final report on Contract BLM JP910C82018 to the U.S. Bureau of Land Management, Salt Lake City Office. 54 p. plus appendices.
- Lapakko, K.A., Antonson, D.A. 2001. Laboratory drainage pH and sulfate release rates from Archean Greenstone rock. In Securing the Future, International Conference on Mining and the Environment. June 25-July 1, Skellefteå, Sweden. p. 384-393.
- Lapakko, K.A., Antonson, D.A. 2002. Drainage pH, acid production, and acid neutralization for Archean greenstone rock. Preprint 02-73 In Proc. 2002 SME Annual Meeting, February 25-27, Phoenix, AZ (CD-ROM). Soc. For Mining, Metallurgy, and Exploration, Inc. Littleton, CO.
- Lapakko, K.A., Antonson, D.A., Johnson, A. 2001. Archean greenstone laboratory and field dissolution experiments. Controlling mine drainage problems - New approaches for waste

- rock stockpiles. Final Report to Minerals Coordinating Committee. 30 June 2001. MN Dept. Nat. Resources, Division of Lands and Minerals, St. Paul, MN. 79 p. plus appendices.
- Lapakko, K.A., Antonson, D.A., Folman, J.T., Johnson, A.M. 2002a. Laboratory drainage quality from mafic-intrusive, tuffaceous-sedimentary, and weathered waste rocks. Final Report on Contract JSP012002 to the U.S. Bureau of Land Management Salt Lake City Office, 30 June 2002. 81 p. plus appendices.
- Lapakko, K.A., Antonson, D.A., Folman, J.T., Johnson, A.M. 2002b. Laboratory drainage quality from Archean greenstone rock. Final report on Contract BLM JSP012002 to the U.S. Bureau of Land Management, Salt Lake City Office. 68 p. plus appendices.
- Lapakko, K.A., Antonson, D.A., Folman, J.T., Johnson, A.M. 2002c. Assessment of test methods for waste rock dissolution and laboratory drainage quality from Duluth Complex rock. Report on Contract BLM JSP012002 to the U.S. Bureau of Land Management, Salt Lake City Office. 63 p. plus appendices.
- Lapakko, K.A., Wessels, J. N. 1995. Release of acid from hydrothermal quartz-carbonate hosted gold-mine tailings. In Sudbury '95, Conference on Mining and the Environment, Sudbury, Ontario, May 28th - June 1st, 1995. p. 139-148.
- Lapakko, K.A., White, W.W. III. 2000. Modification of the ASTM D 5744-96 kinetic test. In Proc. Fifth International Conference on Acid Rock Drainage. SME, Littleton, CO. p. 631-639.
- Lawrence, R. W. 1990. Prediction of the behaviour of mining and processing wastes in the environment. In Mining and Mineral Processing Wastes, Doyle, F. M., (ed.), Proc. Western Regional Symposium on Mining and Mineral Processing Wastes, Berkeley, CA. Soc. Min. Eng. AIME: Littleton, CO. 115-121.
- Lin, C. 1996. Modeling acid mine drainage. University of Utah, Department of Chemical and Fuels Engineering, unpublished Ph.D. dissertation, June 1996. 264.
- Lin, C., Trujillo, E.M., White III, W.W. 1997. A three-dimensional, three-phase geochemical kinetic model for acid rock drainage. In Proceedings of the Fourth International Conference on Acid Rock Drainage, May 30 - June 6, 1997, Vancouver, British Columbia, Canada (in press). 14.
- McCrea, K. 2000. Email from Karl McCrea of American Assay Laboratories, 19 October 2000.
- Mills, C. 1999. Variables and uncertainties in the geochemical characterization of mineral samples by kinetic methods. In Summary Notes 5th Annual BC MEM \_ MEND 2000 Metal Rinseing and ARD Workshop. MEND Program, Vancouver, BC, Dec. 9\_10, 1998. Section C.2, p. 1\_12.
- Morin, K.A., Hutt, N.M. 1999. Humidity Cells: How Many? How Long? In Proceedings of Sudbury '99, Mining and the Environment II. September 12-15, 1999, Sudbury, Ontario, Canada. p. 109-117.
- Morin, K.A., N.M. Hutt, Ferguson, K.D. 1996. The International Kinetic Database: Rates of acid generation, neutralization, and metal Rinseing from mines around the world. In Proceedings of the 3rd International and 21st Annual Minerals Council of Australia Environmental Workshop, October 14\_18, Newcastle, New South Wales, Australia, 1132:148.
- Trujillo, E. M., Lin, C., Leonora, S. 1994. Development of an acid mine drainage model (final report on U.S. Bureau of Mines contract 1432-J02300003). Department of Chemical and Fuels Engineering, University of Utah. 65 p.
- Trujillo, E. M., Lin, C., Guard, F. 1996a. Development of an acid mine drainage model (final report

- on U.S. BLM contract J910P62005). Department of Chemical and Fuels Engineering, University of Utah. 62 pp.
- Trujillo, E. M., Lin, C., Guard, F. 1996b. Humidity cell testing - Lewistown samples (final report on U.S. BLM contract J910P62008). Department of Chemical and Fuels Engineering, University of Utah. 48 pp.
- Trujillo, E. M., Guard, F., Lin, C. 1997. Acid mine drainage-Mathematical Models: Brief literature review of uranium, selenium and arsenic (preliminary report on U.S. BLM contract J910P72013). Department of Chemical and Fuels Engineering, University of Utah. 62 pp.
- Trujillo, E.T., Dumett, M., Guard, F. 1998. Acid mine drainage-Mathematical models (final report on BLM contract J910P72013). Dept of Chemical and Fuels Engineering, University of Utah. 60 pp.
- Trujillo, E.T., Dumett, M., Krishnamoorthy, G. 2000. Prediction of acid mine drainage from waste rock and open pit lakes (final report on BLM contract J910P72017). Dept of Chemical and Fuels Engineering, University of Utah.
- U.S. Bureau of Mines. 1994. Predictive chemical model for acid mine drainage. In Annual Progress Report: Fiscal Year 1994. Salt Lake City Research Center, Salt Lake City, UT. p. 160-169.
- U.S. Bureau of Mines. 1995. Predictive chemical model for acid mine drainage. In Annual Work Plans. Salt Lake City Research Center, Salt Lake City, UT. p. 138-145.
- USFS. 1993. Acid drainage from mines on the National Forests: A management challenge. United States Department of Agriculture, Forest Service, in cooperation with the U.S. Department of Interior's Bureau of Mines Program Aid 1505, March 1993.
- Williamson, M.A., Rimstidt, J.D. 1994. The kinetics and electrochemical rate-determining step of aqueous pyrite oxidation. *Geochim. Cosmochim. Acta*, 58. p. 5443-5454.
- White, W.W. III, Jeffers, T.H. 1994. Chemical predictive modeling of acid mine drainage from metallic sulfide-bearing waste rock. In Environmental Geochemistry of Sulfide Oxidation; ACS Symposium Series 550; American Chemical Society: Washington, DC, 1993. p. 608-630.
- White III, W.W., Lapakko, K.A. 2000. Preliminary indications of repeatability and reproducibility of the ASTM D 5744-96 kinetic test for drainage pH and sulfate release rate. In Proceedings from the Fifth International Conference on Acid Rock Drainage. SME, Littleton, CO. p. 621-630.
- White, W.W. III, Trujillo, E.M., Lin, C. 1994. Chemical predictive modeling of acid mine drainage from waste rock: Model development and comparison of modeled output to experimental data. In Proceedings of the International Land Reclamation and Mine Drainage Conference and the Third International Conference on the Abatement of Acid Drainage, Pittsburgh, PA. p. 157-166.
- White, W. W. III, Lapakko, K.A., Cox, R.L. 1997. Effects of protocol variables and sample mineralogy on static-test NP. In Proceedings of the Eleventh Annual Conference of the Society of Mineral Analysts, April 7-10, 1997, Elko, NV. p. 188-233.
- White, W. W. III, Lapakko, K.A., Cox, R.L. 1999. Static-test methods most commonly used to predict acid mine drainage: Practical guidelines for use and interpretation. In The environmental geochemistry of mineral deposits, Part A: Theory and background, Plumlee, G.

S. and M. Logsdon (eds.). Soc. of Econ. Geol., Reviews in Economic Geology, v. 7A. p. 325-338.